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THE DARPA HIGH-PERFORMANCE POLYMER PROGRAM

Volume I. Program Background and Highlights of the Program Review Held on 14-15 January 1992

David R. Squire, *IDA Consultant*
Loker Hydrocarbon Research Institute
University of Southern California

George Mayer
Institute for Defense Analyses

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FOREWORD

This document was prepared for the Materials Science Division, Defense Sciences Office, Defense Advanced Research Projects Agency, as part of Project Assignment A-131 under the technical cognizance of Dr. Richard T. Loda.

While this document has not been subjected to formal IDA review, it has been read by IDA and DARPA personnel and is believed to be an accurate account.

PREFACE

The Defense Sciences Office of the Defense Advanced Research Projects Agency (DARPA) has conducted a program in high-performance polymers since 1984. A comprehensive review of this program was held on 14-15 January 1992 by Richard T. Loda, the present DARPA program manager, and this report is meant to place that review on record. Volume I of the report covers a brief history of the program, including descriptions of some of the past and pending payoffs, and a discussion of the highlights of the review. Volume II is an appendix which contains selected material from the presentations by the contractors. With this formatting, Volume I is a concise, stand-alone description (basically an executive summary) of the polymer program, while the appendix, Volume II, is a reference source document where details may be found when needed.

ACKNOWLEDGMENT

The authors hereby acknowledge the yeoman service of John E. Hove, of IDA, in reviewing and substantially editing this report.

ABSTRACT

In a series of projects dating back to 1984, the Defense Advanced Research Projects Agency (DARPA) has instigated research in advanced polymers including such goals as thermally oxidatively stable matrix resins for 700°F composite applications, rigid molecular composites, liquid crystal displays, and piezoelectric sensors. Volume I of the present report reviews the history and accomplishments of the DARPA High-Performance Polymer Program and presents highlights of the program review conducted by DARPA on 14-15 January 1992. Volume II, intended as a comprehensive reference source document, is an appendix which provides the program review agenda, a list of participants, and copies of selected presentation material. Correspondence from the presenters is included with the presentation material where appropriate.

CONTENTS - VOLUME I

I. INTRODUCTION AND HISTORY OF THE DARPA HIGH-PERFORMANCE POLYMER PROGRAM

In this volume, this report briefly reviews the history of the polymeric materials program at the Defense Advanced Research Projects Agency (DARPA) and identifies several past or pending payoffs that seem worthy of discussion. It then presents highlights of the DARPA program review conducted 14-15 January 1992 at System Planning Corporation in Arlington, Virginia. Copies of selected material presented at the program review are appended in Volume II.

In the early 1980s, the original push to develop a polymeric materials program at DARPA came from Ben A. Wilcox, Director of the Materials Science Division, Defense Sciences Office. The principal driver was the high-performance composite materials requirements for the Advanced Tactical Fighter (ATF). In 1984, Wilcox brought Phillip A. Parrish on board to oversee the development and implementation of the high-performance polymer program. During this period, with the collaboration of the Air Force, there were two principal thrusts: (1) development of thermally oxidatively stable (TOS) resins that would meet the aircraft industry requirements for 700°F (371°C) composite applications and (2) development of molecular composites in which the reinforcing component is a rigid, long chain molecule molecularly dispersed in flexible coillike molecules.

These programs were quite productive. John Stille at Colorado State University was successful in the synthesis and blending, for the first time ever, of materials that are truly molecular composites, as verified both by physical properties and by x-ray diffraction analyses. These novel materials are based upon the chemistry of polyquinolines. Presently, Maxdem, a company located in Southern California, is promoting their commercialization for electronic packaging.

In the area of TOS polymers, investigators at Hoechst Celanese were successful in developing a resin that is stable to 500°F (260°C) and is both processable and scalable, based upon polybenzimidazole/polyimide (PBI/PI) chemistry. Components made from this resin have higher solvent resistance as well as much higher temperature stability (500°F versus 250°F) than resins presently utilized. James E. McGrath, of the Virginia

Polytechnic Institute, was involved in helping to make this program successful. McGrath has gone on under separate DARPA funding to develop a class of polymeric materials that early results show should perform well in TOS tests at temperatures up to 800°F (427°C). Thus, the DARPA program succeeded in increasing high-temperature oxidation stability far beyond present capabilities.

In 1985, the polymer program at DARPA was markedly enhanced by becoming involved in the University Research Initiative (URI). Through funding provided by this initiative, six major projects were initiated in various areas of polymer research and technology which ranged from basic theoretical investigations to experimental investigations of liquid crystalline polymers and to studies of conducting polymers. While the results of the URI projects are mentioned later, two such projects are worth highlighting here. In one of these, over a 5-year period workers at the University of Pennsylvania and Ohio State University developed a conducting polymer from a laboratory curiosity into a stable material that has now been commercialized (by Hexcel and Allied-Signal). The impact of conducting polyaniline for military systems is extensive and ranges from lightning-strike protection to utilization in honeycomb structures in aircraft. Conducting polyanilines are representative of a new class of materials known as synthetic metals. This technology is still discovering new and varied applications in both military systems and the commercial marketplace.

A second URI-funded DARPA project has led to the development of a highly novel display technology that is based upon liquid crystalline polymers. This new technology is expected to largely displace cathode-ray tube (CRT) technology in this decade, as it will be four times brighter and have higher contrast, greater simplicity, and an unlimited viewing angle. An active transition is now ongoing at DARPA in the high-definition display technology program. This has obvious commercial payoffs and, in an effort along these lines, the National Science Foundation (NSF) recently initiated a Science and Technology Center at Kent State which also involves Case Western Reserve and the University of Akron.

In 1988, one of the authors of this report, David R. Squire, joined DARPA with the charter of developing the Materials Chemistry Program and, in particular, expanding the polymer program beyond the ongoing thrusts and the directions of the URI projects. The new efforts brought about the development of materials with enhanced compressive strength properties, the development of supercritical processing technologies, and the development of advanced composites and coatings.

In 1990, Richard T. Loda joined DARPA. Under his management of the Materials Chemistry Program, the Hoechst Celanese effort on high-temperature resin matrices was pushed to a higher level via the support of McGrath at Virginia Polytechnic. A scale-up and demonstration project for this new class of polymers was initiated with Lockheed and Maxdem. The polycarbosilane project at the University of Southern California was nurtured via additional funding and the inclusion of Hercules, and an electronic packaging demonstration is now undergoing development.

The numerous transitions into other DARPA offices, as well as interested involvement by corporations such as Hercules and Owens Corning, indicate the productivity of the polymer program. In brief, this program has led to the development of the following:

- A new class of polymers that perform structural roles well beyond 700°F (371°C)
- A new class of polymeric piezoelectric sensors
- Electrostrictive polyurethanes for application in advanced sonar technology
- Novel drag-reducing polymers for submarine use that have 10 times the efficiency of presently used materials
- High-performance boron nitride fibers
- Low-cost, high-performance carbon fibers from pitch utilizing supercritical fluid technology
- Novel silicon-carbon polymer for electronic packaging, and
- The successful demonstration of the processing of polymers into fibers utilizing supercritical fluid technology.

II. SELECTED PAYOFFS OF THE ADVANCED POLYMER PROGRAM

This section contains graphical and pictorial presentations of several of the DARPA funded projects that either have transitioned or are on the threshold of transitioning from the laboratory to actual applications and in some instances to industrial commercialization. Charts 1 through 6 are abstracted from the copies of the program review presentations given in Volume II of this report. They are self-descriptive and require no captions. The authors of this report have included these charts here in stand-alone form because they could be useful in further transition efforts either to potential DoD customers or to the commercial sector. The charts are as follows:

Chart Number	Subject
1	Synthetic metals using polyaniline chemistry
2*	High-definition liquid crystal displays
3	Polymeric piezoelectric materials
4	Drag-reducing polymers for ship and submarine use
5**	Novel polycarbosilanes for uses such as electronic module encapsulation
6	Ultra-high-temperature performance organic matrix resins and structural adhesives

* Chart 2 uses but does not define the abbreviations VFD and PDP. VFD stands for vacuum fluorescent displays, and PDP stands for plasma display panels.

** Chart 5 is from the University of Southern California (William P. Weber).

Additional discussions of the six subject areas covered by the charts will be found in Section III.

Chart 1

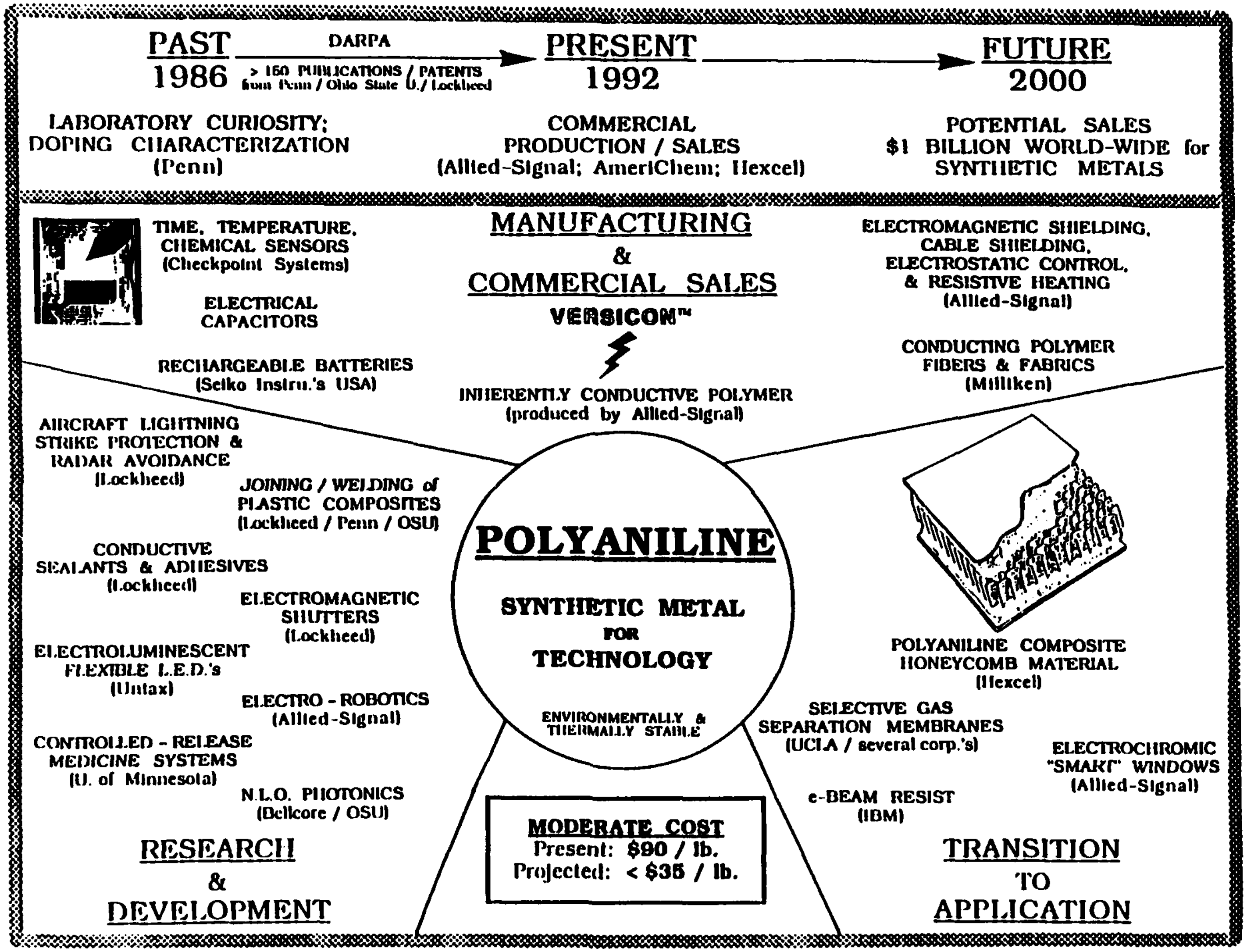

PAST
1986
DARPA
> 150 PUBLICATIONS / PATENTS from Penn / Ohio State U. / Lockheed
PRESENT
1992
FUTURE
2000
LABORATORY CURIOSITY; DOPING CHARACTERIZATION (Penn)
COMMERCIAL PRODUCTION / SALES (Allied-Signal; AmeriChem; Hexcel)
POTENTIAL SALES $1 BILLION WORLD-WIDE for SYNTHETIC METALS
TIME, TEMPERATURE, CHEMICAL SENSORS (Checkpoint Systems)
ELECTRICAL CAPACITORS
RECHARGEABLE BATTERIES (Seiko Instru.'s USA)
MANUFACTURING & COMMERCIAL SALES
VERSICON™
INHERENTLY CONDUCTIVE POLYMER (produced by Allied-Signal)
ELECTROMAGNETIC SHIELDING, CABLE SHIELDING, ELECTROSTATIC CONTROL, & RESISTIVE HEATING (Allied-Signal)
CONDUCTING POLYMER FIBERS & FABRICS (Milliken)
AIRCRAFT LIGHTNING STRIKE PROTECTION & RADAR AVOIDANCE (Lockheed)
JOINING / WELDING of PLASTIC COMPOSITES (Lockheed / Penn / OSU)
CONDUCTIVE SEALANTS & ADHESIVES (Lockheed)
ELECTROMAGNETIC SHUTTERS (Lockheed)
ELECTROLUMINESCENT FLEXIBLE L.E.D.'s (Uniax)
ELECTRO - ROBOTICS (Allied-Signal)
CONTROLLED - RELEASE MEDICINE SYSTEMS (U. of Minnesota)
N.L.O. PHOTONICS (Bellcore / OSU)
RESEARCH & DEVELOPMENT
POLYANILINE
SYNTHETIC METAL FOR TECHNOLOGY
ENVIRONMENTALLY & THERMALLY STABLE
MODERATE COST
Present: $90 / lb.
Projected: < $35 / lb.
POLYANILINE COMPOSITE HONEYCOMB MATERIAL (Hexcel)
SELECTIVE GAS SEPARATION MEMBRANES (UCLA / several corp.'s)
ELECTROCHROMIC "SMART" WINDOWS (Allied-Signal)
e-BEAM RESIST (IBM)
TRANSITION TO APPLICATION

Chart 2

ADVANCED DISPLAY MATERIALS

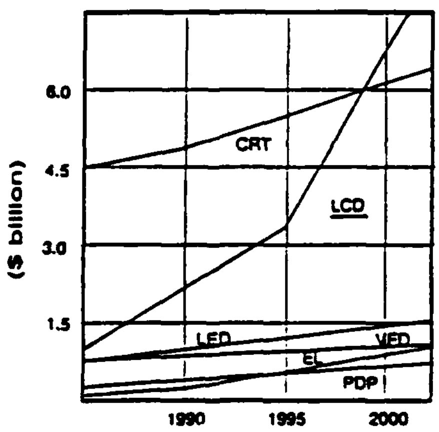
Through the support of DARPA and more recently NSF, Kent State University has taken a leadership role in advancing liquid crystal materials for displays and other electro-optic applications. The most important discoveries have come from the combination of liquid crystals and polymers in the form of dispersions. These materials have led to displays with improved brightness and contrast as well as simplified electric drive schemes at reduced cost. They also make possible new kinds of products such as electrically switchable windows for solar and privacy control.

The Kent program has resulted in some dozen patents (issued or filed) which have been licensed to both small companies (e.g., Polytronix Corp.) and large industries (e.g., General Motors) for product development. Kent's strong patent position on dispersed liquid crystals contributes to U.S. competitiveness in a fiercely competitive international display market. The significance of liquid crystal displays (LCDs) in the world market (see market prediction below) shows that LCD flat-panel displays in general will dominate before the turn of the century.

The possibilities for new and improved dispersions appear endless at this stage of development. For example, a new type of dispersion involving polymer gels was recently discovered at Kent under DARPA University Research Initiative and High Definition Display programs. In reflective displays the new material produces brilliant colors with a contrast exceeding current technology by a factor of five. Gel dispersions create bistable states in the liquid crystals; the result is high resolution displays with simplified electronic drive circuitry.

Displays under development using dispersions:

- High intensity projection systems
- Large wall-size front-lit displays with memory
- Head-up displays
- High-resolution front-lit flat-panel displays



Projected display market (from *DISPLAY DEVICES '90*) illustrating the growth of various technologies: cathode ray tube (CRT), liquid crystal display (LCD), light emitting diode (LED), and electroluminescence (EL).

Chart 3

POLYMER ELECTROPROCESSING LABORATORY

Rutgers, The State University of New Jersey
Co-Directors: Jerry I. Scheinbeim & Brian A. Newman

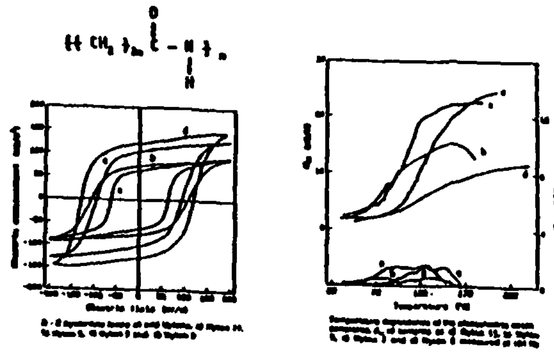
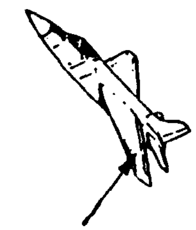
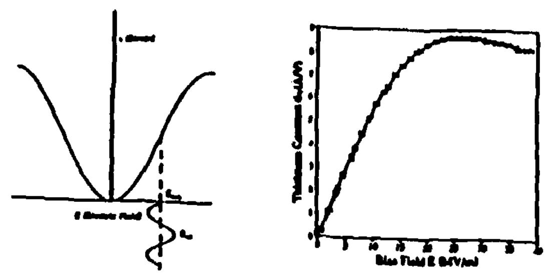
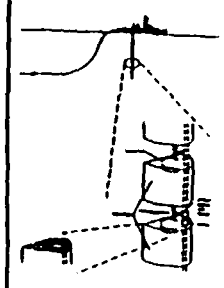
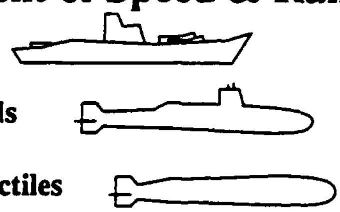
Materials Need:	Polymer Electroprocessing Laboratory Approach:	Applications // *Transition:*	Estimated Markets:
I) A piezoelectric polymer which can operate at temperatures ≥ 200° C.	Discover and develop a new class of high temperature stable ferroelectric/piezoelectric polymers - the odd numbered nylons. 	1) embedded in 200° C cured polymer composite materials as stress/strain/failure sensors. 2) smart skins 3) tough, engine compartment piezoelectric sensors. 4) high temperature, tough, inexpensive, piezoelectric moisture sensors. ***Atochem Sensors is licensing odd number nylon piezoelectric technology and developing prototype sensors and circuits.***	Atochem Sensors estimate 50-100 million dollars.  Piezoelectric nylon 5 sensors embedded in advanced composite wing (cured above 200° C)
II) A piezoelectric material with thickness coefficient, $d_T \geq 5$ Å/V and a modulus ~10^7 N/m².	Create and develop a new class of "apparent" piezoelectric materials using high D.C. biased electrostrictive materials. Example: the polyurethanes  Basic electrostrictive response. d_T of a polyurethane as a function of D.C. bias field.	Basis for Acoustics Radiator for Tactical Search(ARTS) program - DARPA funded program for developing a new low frequency sonar projector rests on our discovery of the enormous response of electrostrictive polyurethanes (d_T=45 Å/V, static strains~20%) ***SRI is developing the prototype acoustic projector (low frequency sonar projector).***	DARPA/SRI estimate 1-7 billion dollars.  Acoustic radiator for tactical search

Chart 4

POLYMERIC DRAG REDUCTION
FOR MARINE APPLICATIONS

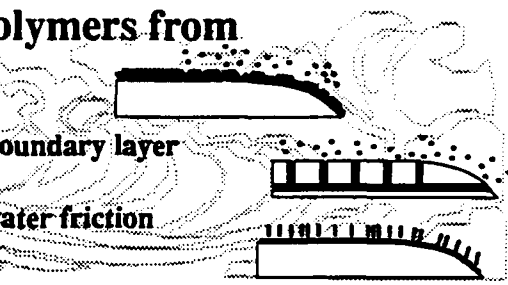
40% Enhancement of Speed & Range of

- √ Surface Vessels
- √ Submerged Vessels
- √ High Speed Projectiles



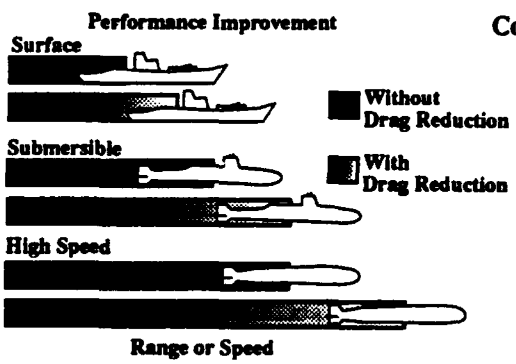
With Drag Reducing Copolymers from

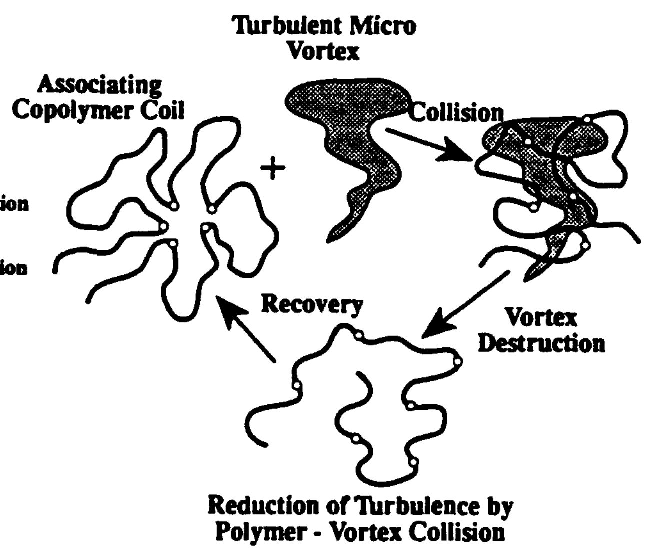
- √ High-speed fluid shear removal
- √ Regulated addition to surface boundary layer
- √ Surface attachment to reduce water friction



With Superior Properties that

- √ Give greater drag reduction that traditional homo-polymers
- √ Can be tailored for environmental needs
- √ Resist shear degradation
- √ Can alter acoustical signature





The University of Southern Mississippi
Department of Polymer Science

Chart 5

NEW HIGH PERFORMANCE MATERIALS FROM POLY(CARBOSILANES)

1988	1989	1990	1991	1992
Began Synthesis of Novel Si-C Materials	Patents Developed with Hercules	Six Patents Filed/One Granted		Development of Applications

Si-C

Electronic Encapsulant Materials

- Reliability without Hermaticity
- Tg is >150° C
- Stable to Thermal Shock (-50 to 150° C)
- Low Dielectric ~2
- Low Moisture Adsorption 0.01%

Corrosion Barrier Coatings

- Low Moisture Adsorption 0.01%
- Low Chloride Ion Content

Composite Materials

- Ease of Coating (Prepreg) Carbon Fabric
- Standard Low Temperature Thermal Cure
- No Volatiles
- Strength in Compression
- Low Dielectric Circuit Boards

Performance Comparisons

	-Si-C- (new material)	Polyimides (candidate)	Expoxy (currently used)
Dielectric Constant	2.0	2.8-3.5	3.6-4.1
Moisture Uptake %	0.01	0.8-2.0	2-3
Dissipation Factor	0.002	0.002-0.01	0.01
Coefficient of Thermal Expansion	30	20-38	22

Novel -Si-C- materials are easily processable, coat microstructures easily, and there is no gas evolution on curing.

Chart 6

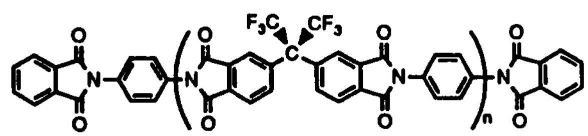
ULTRA HIGH TEMPERATURE PERFORMANCE ORGANIC MATRIX RESINS AND STRUCTURAL ADHESIVES

Virginia Polytechnic Institute and State University

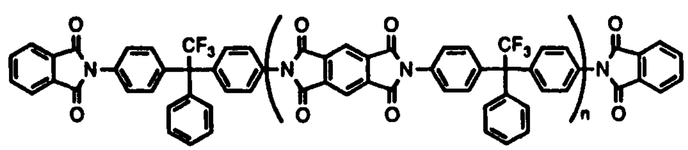
1987	1989	1990/1991	1992
• Initiation of Blending of PBI/PI Hoechst Celanese/GE Lockheed	• Inclusion of University of Massachusetts and VPI Investigators in Project • End Capping, 3F and 6F Polyimides (Tg = 350°C and 314°C) Introduced	• Achieved 500°F TOS PI/PBI Blends • Rear Access Door Demonstration	• Introduction of PMDA - 3F Diamine Polyimide Tg = 440°C • Fabrication into Aircraft Engine Bushings Achieved with Testing at GE • Introduction of Phosphine Oxide Polymer, Tg ≤ 430°C

STRUCTURES

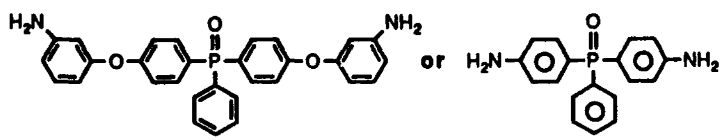
6F-pPD-PA



PMDA-3Fdiamine-PA



mBAPPO



ACCOMPLISHMENTS AND APPLICATIONS

- *Prototype Engine Bushings Tested*
- Structural Adhesives - 6000 psi lap shear to titanium achieved
- Superior Solar Blankets
- Fire and Oxygen Plasma Resistant Materials
- Potential for Titanium Replacement in F-22 and Other Aircraft
- Potential for Development of High Performance Turbine Engine Development
- Potential for Electronic Packaging/NLO

III. HIGHLIGHTS OF THE DARPA REVIEW OF THE HIGH-PERFORMANCE POLYMER PROGRAM

The DARPA Program Review was held on 14-15 January 1992 at the facilities of the System Planning Corporation in Arlington, Virginia. The agenda and the list of participants are given in Section IV. Copies of selected presentation charts are included in Volume II. Selected technical highlights of the presentations are given below, along with comments by the authors of this report. University Research Initiative programs are identified by the abbreviation URI in the headings.

A. UNIVERSITY OF MASSACHUSETTS (KARASZ) - URI

These researchers have made substantial headway in the development of new characterization techniques including quasi-elastic light scattering (QELS) and forced Rayleigh scattering (FRS) for investigating diffusion in polymers. Their studies of phase relations in polymer blends should impact polymer blend development via enhanced, tailored performance.

B. UNIVERSITY OF MASSACHUSETTS (MIT/THOMAS) - URI

The program under Ned Thomas has led to the discovery of how to make, in a controlled manner, highly oriented microcomposites with unique structures and morphologies. Thomas has successfully scaled up the method to make large samples (5 inches square) in which the microstructure can be oriented in a flow field, nucleates and self-assembles, and yields a single crystal with no grain boundaries. This control of morphology at the microlevel provides a pathway to make high-strength polymers for which the stress-strain behavior can be tailored. This also presents an opportunity to explore the making of thick-section composites using his oscillating shear method. It may be possible to utilize the technique and a back-and-forth rastering procedure that will enable the making of large panels or sections of curvature. Prior to fabrication of large sections, a key issue will be the determination of compressive characteristics.

C. UNIVERSITY OF MASSACHUSETTS (FOSTER-MILLER/ BLIZARD) - URI

Ultra-high-performance blends have been made by using a novel melt processing method that requires no solvents and that can easily be scaled up. This new method uses a twin-screw extruder that operates in the 300-400°C temperature range. It will have applications such as making injection-molded parts and making thermoplastic resins for graphite composites that should be stable to temperatures 150°C higher than epoxy. The broader utility of these developments should be evaluated by the services.

D. UNIVERSITY OF PENNSYLVANIA (MacDIARMID) - URI

The first commercialized conducting polymer, manufactured by Hexcel and Allied-Signal, and based on the technology of polyanilines, resulted directly from this program. Widespread military uses are under active study, including replacement of metal in honeycomb structures, conducting adhesives for airframe applications, and conducting coatings for lightning dissipation on aircraft structures. These accomplishments are remarkable in that they brought a laboratory polymer to commercialization in less than 5 years.

High-molecular-weight polyanilines have led to a factor-of-3 improvement in conductivity. Further, blending may lead to an improvement in conductivity by an order of magnitude greater than that for pure polyaniline. The investigation of stretched orientation of polyanilines has resulted in tensile strengths above 300 ksi. Other processing methods that use zone drawing and film casting have also been successful in achieving high orientations that will lead to the development of conducting polymers with excellent mechanical properties.

[Authors' comment: It is suggested that an analysis be conducted to determine the possibility of using conducting polymers in batteries as current collectors, which would lighten the batteries significantly by replacing nickel. Electrically conducting polymers may also find application in fuel-cell developments by providing highly conducting access routes from catalyst sites to electrodes, in effect greatly enhancing electron mobility in both the anode and the cathode. These techniques, as well as synthesis and processing, need to be explored to fully exploit the high electronic conductivity of these polymers.]

E. UNIVERSITY OF PENNSYLVANIA (OHIO STATE/EPSTEIN) - URI

These researchers have discovered that the key to high conductivity is interchain interactions which prevent electron reflection via defects.

Microwave investigations of processing and welding using polyanilines are promising. The advantage of polyanilines is that they act as self-regulating heating elements, preventing thermal runaway. The researchers are presently extending their microwave studies on polymers and blends via investigations of controlled weldability of thermoplastic joints using polyanilines and blends.

Use of polyanilines as biosensors and/or chemical sensors may be possible through electrochemical control of enzyme activity. Sensor work is now under development with Allied-Signal.

[Authors' comment: Exploratory investigations using microwave processing through conducting polymers for joining thermoplastics give promising results and, in particular, avoid thermal runaway difficulties. Welding studies using polyaniline as the adherend have proven successful and have resulted in bond strengths (3000 psi) double those of the prior materials (1500 psi). Fabrication processes, field repair, and time savings may result, as the method is exceptionally fast compared to conventional epoxy methods.]

F. UNIVERSITY OF PENNSYLVANIA (KENT STATE/WEST) - URI

This program in liquid crystalline polymers has led to advances in display technology that are very likely to displace CRT technology in this decade. These researchers have developed displays with unlimited viewing angle, brightness four times that of a CRT, faster response, and higher contrast, as well as lower cost and greater simplicity. The results of this program are being considered for commercialization via joint ventures and are also being transitioned via the High-Definition Display (HDD) Program at DARPA.

The researchers have also developed smart switchable windows that are entering the process of being commercialized. For the military, these developments mean access to brighter and easier to view head-up displays and the possibility of smart canopies and radomes. This is another example of a research opportunity which has transitioned from one DARPA office (Defense Sciences Office, DSO) to another DARPA program (HDD).

G. MIT (COHEN) - URI

This theoretical program has, for the first time, enabled quantitative, atomic-level, first-principles investigations of the origins of plastic deformation in polymeric materials and the prediction of its onset, as well as providing the capability of predicting the mechanical properties of glassy polymers. This fundamental insight could eventually permit the tailoring of polymer systems to have the desired physical properties and to lead to better control of their processing texture formation.

These investigators have determined elements of structure that enhance plastic flow (ductile) versus crazing (premature brittle fracture), which in turn relates closely to issues of aging and embrittlement through atomic-level modeling and design. It was discovered that plastic flow in glassy polymers is by shear. Shear transformations are usually dilatant in nature and thus generate additional free volume. One of the most significant findings resulting from this research is the determination that long-range forces can be attributed to short-range effects. Long-range cooperative motion is extremely important in any analysis at the molecular level.

H. UNIVERSITY OF TEXAS, ARLINGTON (POMERANTZ) - URI

This program has led to the development of a stable and processable conducting polymer, polypyrole, that is compatible with aircraft composites. A fully integrated dipole antenna has been made and successfully tested. This antenna is quite thin and can be incorporated in the surface of an aircraft. These conducting polymers have low band-gaps and are also transparent. They could be considered as candidate materials for fuel-cell and battery applications.

I. UNIVERSITY OF ILLINOIS (ECONOMY)

Synthesis of high-performance B-N fibers has been developed and has led to fibers that have thermal-oxidative stability to 850°C, low dielectric constant (4.0), and should have improved compressive behavior, as the fibers have no microfibrillar morphology, present no accidental release problems (as do carbon fibers), and are stable in metal and ceramic matrices. Starting materials are very low in cost (cents per pound), and a high yield can be obtained (70%). Scale-up of synthesis and processing is being effected by teaming with Owens-Corning Fiberglas; uniform fibers have already been synthesized with diameters of 3, 4, and 6 microns. A dodecane sizing has also been developed that protects the fiber from moisture and provides handling ease. A new process development includes incorporating a small quantity of silica that extends the temperature stability to 950°C.

J. UNIVERSITY OF ILLINOIS (ECONOMY)

Progress has been made in using polymers that take advantage of a transesterification reaction to form the final product rather than an epoxylike reaction. The researchers are close to realizing their goal, which is high-modulus polymer materials exceeding epoxies for better supporting structures, and use temperatures higher than those of epoxies by 150-200°C. This enables solid-state forming, as no gaseous by-products are formed in the final step. These polyesters should have applications as high-temperature adhesives for bonding aluminum, steel, and titanium. Uses as structural foams, as dielectric insulators, and as corrosion-resistant coatings are other applications. This research is being coupled with industrial partners in FY92.

K. RUTGERS UNIVERSITY (SCHEINBEIM)

Researchers have developed a new class of piezoelectric polymers that is based on odd-numbered nylons. These odd nylons have extraordinary thermal stability as compared to polyvinylidene fluorides (PVF2), which degrade in the 100-135°C range. The odd nylons have stabilities ranging from 185°C for Nylon 11 to 260°C for Nylon 5. Further, the investigators discovered that a blend of PVF2 with an odd nylon has a higher piezoelectric response than the sum of the two components. Uses being explored include sensors built into fiber-reinforced epoxy composites that will sense fatigue and other damage. The researchers have also developed a piezoelectric material that has twice the electromechanical coupling coefficient of the best to date.

Their research has developed polyurethane films that are electrostrictive with properties that should enable the development of highly novel sonar receivers and transmitters that can operate below 100 Hz. A prototype sonar device is now being built in conjunction with the Undersea Warfare Office at DARPA.

L. UNIVERSITY OF CALIFORNIA (WEBER)

A novel class of polymers derived from Si-C chemistry rather than siloxane chemistry has been developed that has properties and processability which have potential for electronic packaging. These properties include very low moisture absorption, no transport of water, and thermal stability. The dielectric constant is quite low (about 2.0). A prototype demonstration is in process and is being done cooperatively with Hercules and DoD packaging experts. This technology will enable the production of circuit-board laminate components that have low dielectric constants, dimensional stability, and improved resistance to cracking on thermal cycling. [*Authors' comment: It is recommended that transitioning to the Electronic Systems Technology Office of DARPA be explored.*]

M. UNIVERSITY OF SOUTHERN MISSISSIPPI (McCORMICK)

These investigators have not only made advances in developing insight into the mechanism of action of drag-reduction polymers, but have also developed a quantitative method and a test procedure for comparing relative drag-reducing efficiencies of polymers. Further, they have developed a copolymer of acrylamide that appears to have an order-of-magnitude improvement in efficiency over polyethylene oxide, which is considered to be the baseline material. Their work has the potential for having high military importance. [*Authors' comment: In order to more fully determine these possibilities, more information is needed, including:*

1. *What are the present requirements in the Navy for drag reduction in surface ships, submarines, and torpedoes? Specifically:*
    a. *Volume and weight of fluids now or projected to be carried on board. Compare McCormick's result with these estimates of weight and volume reduction.*
    b. *Cost projection to compare McCormick's material system with what is being used now (or projected for the future).*
    c. *General logistic and operational problems.*
2. *Other return on investment:*

    Reduction in materials screening cost. Find out what costs are now; projected costs of McCormick's test method.
3. *Calculate drag reduction effects on mission performance for:*
    a. *Fuel conservation in peacetime.*
    b. *Performance enhancement in warfare scenarios for*
        i. *surface ships*
        ii. *submarines*
        iii. *torpedoes.*
4. *Acoustic signal reduction calculations.*
5. *Can nonsacrificial polymers be bonded to surfaces?*

Most of this information is classified, and the authors have not made any effort at such an analysis. They strongly recommend that somebody undertake this study.]

N. HOECHST CELANESE (GLICK)

This team of investigators has successfully made high-temperature oxidation-stable resin to 500°F (260°C) that is processable and scalable and that is based on the polybenzimidazole/polyimide (PBI/PI) system. A 100 lb batch of the 10:90 resin was made and was used to make a high-performance composite component, a rear-access door for the TR1 aircraft, by means of autoclave molding. The resin in this component has much higher solvent resistance as well as much higher temperature stability than resins presently utilized.

These blends, based on PBI/PI, were investigated to overcome some of the inherent problems of PBI and 6F compounds. End capping helped to solve blending problems with Ultem.[1] The researchers have increased T_g so that it now exceeds 300°C; materials are easy to process and have low moisture uptake. However, they exhibit only moderate solvent resistance and are expensive. A more feasible approach that is an outgrowth of this effort is the program now being directed by McGrath at VPI, which has the potential for developing 800°F (427°C) materials.

O. UNIVERSITY OF SOUTHERN CALIFORNIA (AMIS)

For the first time, supercritical fluids have been explored and developed for their unique polymer processing potential (as distinct from fractionation) derived from their extraordinary solvent properties. As much as 10 or more times the weight of polymer can be in solution versus conventional solvents. This enables both blending normally incompatible polymers and eliminating residuals, while dramatically speeding processing. Yields that had been of the order of a few percent have been increased by an order of magnitude. Fibers have been made successfully, and more complex systems will be

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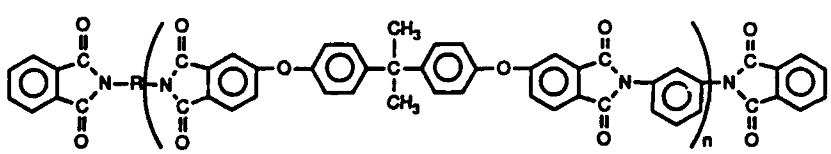
1 Ultem 1000 is a polyether imide with the following chemical structure:



explored, including high-performance fibers, mutually entangled networks, and inorganic-organic networks.

P. VPI (McGRATH)

This program follows on the successes that McGrath helped to bring to the Hoechst Celanese project that had the goal of developing a highly processable high-performance matrix resin with thermal oxidative stability to 700°F. As indicated above in Section III-N, success to 500°F was achieved and a rear-access door demonstration resulted. Under this new program, McGrath has successfully explored new and modified polyimides, processable polybenzoxazoles and new polyimide-modified polyarylene ethers. Already dramatic results have been achieved with the development of PMDA-3F diamine polyimide, which has a glass transition temperature of 842°F (450°C). Prototype engine bushings have been made and are now being tested at General Electric. Lockheed and Maxdem are currently scaling up some of the materials to kilogram quantities to allow for further measurements. Semicrystalline polyimides have also been prepared to investigate the influence of morphology on long-term thermo-oxidative stability (TOS).

McGrath is also developing new processing technology to enhance the processing of polymers with ultrahigh glass transition temperature that is based on the use of fine particles. He has discovered that small-particle dry blends of polymer/metal or polymer/ceramic materials allows direct molding fabrication with the added benefit of eliminating toxic solvents in composites processing.

The VPI team has just recently introduced a new class of high-temperature-stable phosphine oxide polymers that are extremely stable to oxidation. This new class of materials deserves further exploration in view of their outstanding T_g values and fire/oxygen plasma resistance. They also have potential in metal complex hybrid systems.

Q. CLEMSON UNIVERSITY (THIES)

The investigators in this program may have achieved a breakthrough. They have made a high-quality carbon fiber from pitch using supercritical fluid technology for fractionation of the pitch. Composition of the mesophase pitch influences the properties of the resulting carbon fiber. Initial results on fibers made by supercritical fluid (SCF) extraction have resulted in fibers with strengths exceeding those of the best-known pitch-based fibers (Mitsubishi).

Additional emphasis on impurity removal is needed. Sensitivity analysis needs to be done to sort out key variables needing control. These fibers are finding widespread applications in aerospace as well as other industries such as automotive. It remains to optimize the process. This could lead to a low-cost method of making pitch-based high-performance carbon fibers, since petroleum pitch is very inexpensive. It also offers the opportunity for increased reproducibility. A domestic source of high-performance, low-cost carbon fibers is of strategic importance to DoD.

R. RESEARCH TRIANGLE INSTITUTE (PRESTON)

A new high-temperature resin based on ortho linkages in the polymer molecule has been developed with oxidative stability in the 350-400°C range. The investigators have also discovered a new high-strength fiber that is easy to process. Hopefully, more specific data on properties performance will be provided during the forthcoming months.

IV. PROGRAM REVIEW AGENDA AND PARTICIPANTS

The agenda for the 14-15 January 1992 DARPA Review of the High-Performance Polymer Program follows, as does the list of participants. Selected copies of the presentations are appended in Volume II of this report.

DARPA POLYMER PROGRAM REVIEW--JANUARY 14-15, 1992

TUESDAY, JANUARY 14

8:30-8:35	Welcoming Remarks	Ben A. Wilcox, Deputy Director Defense Sciences Office, DARPA
8:35-8:45	Introductory Remarks	Richard T. Loda, Program Manager
8:45-10:00	Univ. of Massachusetts (Karasz)	Chair, Charles Lee, AFOSR
10:00-10:15	BREAK	
10:15-12:15	Univ. of Pennsylvania (MacDiarmid)	"
12:15-1:00	LUNCH	
1:00-2:15	M.I.T. (Argon)	Chair, JoAnn Milliken, NRL
2:15-3:30	Univ. of Texas, Arlington (Pomerantz)	"
3:30-3:40	ADJOURNMENT	
3:45-5:00	Closed Advisory Session	Chair, Richard T. Loda

WEDNESDAY, JANUARY 15

8:30-9:30	Univ. of Illinois (Economy) (2)	Chair, Kenneth Wynne, ONR
9:30-10:15	Rutgers University (Scheinbeim)	"
10:15-10:30	BREAK	
10:30-11:15	Univ. of Southern California (Weber)	"
11:15-12:00	Univ. of Southern Mississippi (McCormick)	"
12:00-12:20	Hoechst Celanese (Glick)	"
12:20-1:00	LUNCH	
1:00-1:45	Univ. of Southern California (Amis)	Chair, Andrew Crowson, ARO
1:45-2:30	VPI and State University (McGrath)	"
2:30-2:45	BREAK	
2:45-3:30	Clemson University (Thies)	"
3:30-4:15	Research Triangle Institute (Preston)	"
4:15-4:20	ADJOURNMENT	
4:20-5:00	Closed Advisory Session	Chair, Richard T. Loda

DARPA Polymer Program Review
January 14-15, 1992

Professor Eric J. Amis
University of Southern California
Dept. of Chemistry, SSC 705
Los Angeles, CA 90089-0482
213-740-4113

Dr. Patrick Aubourg
Owens-Corning
2790 Columbus Road
Granville, OH 43023
614-587-7604

Dr. Edward Balizer
Navy Laboratory White Oak (NSWC)
Silver Spring, MD 20903-5000
301-394-1444

Dr. Kent G. Blizard
Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196
617-290-0992

Dr. Robert Boschan
Lockheed Aeronautical Systems Co.
Dept. 73C4, Zone 0150, Bldg. B1M
86 South Cobb Drive
Marietta, GA 30063
404-494-9714

Dr. Robert F. Brady
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6123
Washington, DC 20375-5000
202-767-2668

Dr. Leonard J. Buckley
Naval Air Development Center
Code 6064
Warminster, PA 18974
215-441-2823

Dr. Edward Chen
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-4325

Dr. Edward C. Chenevy
Hoechst Celanese
86 Morris Avenue
Summit, NJ 07901
908-522-7806

Professor Robert E. Cohen
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139-4307
617-253-3777

Dr. Andrew Crowson
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-4261

Dr. Ronald DeMarco
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000
703-696-5075

Dr. Mark A. Druy
Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196
617-290-0992

Dr. James Economy
University of Illinois
1304 W. Green Street
Urbana, IL 61801
217-333-1440

Professor Ronald L. Elsenbaumer
University of Texas at Arlington
Dept. of Chemistry, Box 19065
Arlington, TX 76019
817-273-3809

Professor Arthur J. Epstein
Ohio State University
Dept. of Physics
174 West 18th Avenue, Room 4108
Columbus, OH 43210-1106
614-292-1133

Professor William A. Feld
Wright State University
Chemistry Dept.
Dayton, OH 45435
513-873-2511

Dr. Morton M. Glick
Hoechst Celanese
86 Morris Avenue
Summit, NJ 07901
908-522-7768

Professor Roger D. Hester
University of Southern Mississippi
Box 10076, Southern Station
Hattiesburg, MS 89406
601-266-4868

Dr. G. Ronald Husk
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-4203

Dr. Brian Jensen
NASA Langley Research Center
MS 226, NASA-LaRC
Hampton, VA 23665
804-864-4271

Professor Frank E. Karasz
University of Massachusetts
Polymer Science Dept., 701 GRT
Amherst, MA 01003
413-545-4783

Dr. Teddy M. Keller
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-3095

Dr. Oh-Kil Kim
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-2088

Dr. Charles Lee
AFOSR/NC
Bolling AFB, DC 20332
202-767-4963

Dr. Raymond Leibfried
Hercules Research Center
Wilmington, DE 19894
302-995-3126

Dr. George A. Lo
Lockheed Missiles and Space Co.
3251 Hanover Street, Polymer Chemistry
Palo Alto, CA 94304-1191
415-424-2504

Dr. Richard T. Loda
Defense Advanced Research Projects Agency
3701 North Fairfax Drive - DSO
Arlington, VA 22203-1714
703-696-2283

Professor Alan G. McDiarmid
University of Pennsylvania
Dept. of Chemistry
343 Chemistry Building
Philadelphia, PA 19104-6323
215-898-8307

Professor William J. MacKnight
University of Massachusetts
Polymer Science Dept., 701 GRT
Amherst, MA 01003
413-545-0433

Dr. George Mayer*
Insitute for Defense Analyses
1801 N. Beauregard Street
Alexandria, VA 22311-1772
703-578-2864

Professor Charles L. McCormick
University of Southern Mississippi
Box 10076, Southern Station
Hattiesburg, MS 89406
601-266-4872

Professor James E. McGrath
Virginia Polytechnic Institute & State Univ.
2111 Hahn Hall, Mail Stop 0212
Blacksburg, VA 24061-0212
703-231-5976

Dr. JoAnn Milliken
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-3088

Professor Brian A. Newman
Rutgers University
Dept. of Materials Science & Engineering
P.O. Box 909
Piscataway, NJ 08855-0909
908-932-4337

Mr. Joe Piche
Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196
617-290-0992

Professor Martin Pomerantz
University of Texas at Arlington
Dept. of Chemistry, Box 19065
Arlington, TX 76019
817-273-3811

* Now at University of Pittsburgh.

Dr. Jack Preston
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194
919-541-6384

Professor John R. Reynolds
University of Florida
Dept. of Chemistry
Gainesville, FL 32611
904-392-9151

Dr. Terry L. St. Clair
NASA Langley Research Center
MS 226, NASA-LaRC
Hampton, VA 23665
804-864-4273

Professor Jerry I. Scheinbeim
Rutgers University
Dept. of Materials Science & Engineering
P.O. Box 909
Piscataway, NJ 08855-0909
908-932-3669

Dr. Michael Sennett
Army Materials Technology Laboratory
Arsenal Street, SLCMT-EMP
Watertown, MA 02172-0001
617-923-5122

Dr. Desmond Sheehan
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-2336

Dr. Arthur W. Snow
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-5341

Dr. David R. Squire
University of Southern California
Loker Hydrocarbon Research Institute
University Park
Los Angeles, CA 90089-1661
213-740-6678

Professor Vivian T. Stannett
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194
919-541-6384

Professor Mark C. Thies
Clemson University
Dept. of Chemical Engineering
Clemson, SC 29634
803-656-3056

Professor Edwin L. Thomas
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139
617-253-6901

Professor William P. Weber
University of Southern California
Loker Hydrocarbon Research Institute
University Park
Los Angeles, CA 90089-1661
213-740-5961

Dr. John West
Kent State University
Liquid Crystal Institute
Dept. of Chemistry
Kent, OH 44242-0001
216-672-2581

Dr. Ben A. Wilcox
Defense Advanced Research Projects Agency
3701 North Fairfax Drive - DSO
Arlington, VA 22203-1714
703-696-2241

Dr. Wen-li Wu
National Institute of Standards and Technology
Building 224, A209
Gaithersburg, MD 20899
301-975-6839

Dr. Kenneth Wynne
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000
603-696-4409

Mr. Joseph Zegarski
Lockheed Missiles and Space Co.
3251 Hanover Street, Polymer Chemistry
Palo Alto, CA 94304-1191
415-424-2192